



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US95/04280  <b>(22) International Filing Date:</b> 7 April 1995 (07.04.95)  <b>(30) Priority Data:</b> 08/225,179           8 April 1994 (08.04.94)       US 08/418,083           6 April 1995 (06.04.95)       US  <b>(71)(72) Applicants and Inventors:</b> ESPOSITO, Anthony, S., Jr. [US/US]; 5218 West Beach Avenue, McHenry, IL 60050 (US). ANDERSON, Michael, C. [US/US]; 5004 St. Joseph Court, Wonder Lake, IL 60097 (US).  <b>(74) Agents:</b> MUNDAY, John, S. et al.; Munday & Stanton, Suite 100, 3434 Garrett Road, Drexel Hill, PA 19026 (US).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).  <b>Published</b> <i>With international search report.</i> <i>With amended claims and statement.</i>
<b>(54) Title:</b> ELASTOMER  <b>(57) Abstract</b>  <p>An elastomeric composition comprising a blend of a block copolymer having terminal polystyrene units and olefin elastomeric midblock units and an ethylene alpha-olefin polymer. The ethylene alpha-olefin polymer preferably has a hardness of from about 65 to about 85 Shore A. In a preferred embodiment, the ethylene alpha-olefin polymer is a substantially linear olefin polymer characterized as having a) a melt flow ratio, <math>I_{10}/I_2 \geq 5.63</math>; b) a molecular weight distribution, <math>M_w/M_n</math>, defined by the equation <math>M_w/M_n \geq (I_{10}/I_2) - 4.63</math>, and c) a critical shear stress at onset of gross melt fracture of greater than about <math>4 \times 10^6</math> dyne/cm<sup>2</sup>. The substantially linear olefin polymer may be further characterized as a copolymer of ethylene with a C<sub>3</sub>-C<sub>20</sub> alpha-olefin. The preferred block copolymer is selected from SEBS, SBS, SEPS and SIS. A preferred composition includes a plasticizing quantity of processing oil, ranging from 0 to 1000 parts of oil per 100 parts of elastomer, and preferably 20 to 200 parts of oil per 100 parts of elastomer. The preferred processing oil is selected from mineral oil, paraffinic oil and naphthenic oil and liquid polybutene oil.</p>		

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**ELASTOMER****TECHNICAL FIELD**

5           This application is a continuation-in-part of an application  
entitled ELASTOMER, filed April 8, 1994, having Serial No.  
08/225,179. The present invention relates to an elastomer having  
improved properties, and more particularly to an elastomer  
employing an ethylene alpha-olefin polymer in combination with  
10 softer block copolymers and oils that maintains the softness of the  
block copolymers while substantially improving the mechanical  
integrity of the elastomer. The invention also relates to formulations  
in which the oil component is substantial.

## **BACKGROUND ART**

Block copolymers such as the Kraton series of polymers having terminal polystyrene units and olefin elastomeric midblock units are used in a wide variety of formulations to produce elastomers for various purposes. Most of the time, the block copolymers, as they are generically known, are modified by or combined with other materials in order to modify some or all of the properties of the block copolymer. For example, oil is often added to function as a plasticizer. Chen U.S. Patent No. 4,369,284 is the first of several Chen patents that disclose a composition consisting essentially of certain Kraton type block copolymers mixed with oil resulting in gelatinous materials that have certain desired properties. Other similar block copolymers such as other forms of Kraton are also shown as not providing those improvements when mixed with oil as disclosed in Chen.

Polypropylene and other polyolefins are often added to improved desired properties of block copolymers. These materials often times improve many of the properties of the block copolymers but bring with them the characteristics of the modifying agent. Polypropylene, for example, improves block copolymer physical integrity and processability but substantially increases the hardness of the resulting elastomeric compound.

A new class of compounds has been patented recently, being generically called ethylene alpha-olefin polymers. Such polymers are described in U.S. Patent No. 5,272,236 and U.S. Patent No. 5,278,272, both to Lai et al. These two patents generally describe elastic substantially linear olefin polymers and characterize them by

properties of the polymers such as melt flow ratio, molecular weight distribution, critical shear rate at onset of surface melt fracture and the like. The ethylene alpha-olefin polymer compounds are said to produce useful compositions by combining the substantially linear  
5 ethylene alpha-olefin polymers with at least one other natural or synthetic polymer. Preferred other polymers listed are thermoplastics such as styrene-butadiene block copolymers, polystyrene (including high impact polystyrene), ethylene vinyl alcohol copolymers, ethylene ethylene acrylic acid copolymers, other  
10 olefin copolymers (especially polyethylene copolymers) and a number of other materials. No specific examples of such useful compositions are disclosed. These ethylene alpha-olefin polymers are also known as metallocenes.

This new class of compounds, herein referred to as  
15 ethylene alpha-olefin polymers, are described as polyolefin elastomers that are extrudable, moldable, and formable. Typical properties of these ethylene alpha-olefin polymers are: density between 0.864-0.935; 100% modulus between 150-750 psi; elongation between 700-1000%; melting point between 50-70 °C; and hardness between 65-  
20 85 Shore A.

Nothing in the prior art suggests that these ethylene alpha-olefin polymers would solve any of the problems of current block copolymer formulations. The ethylene alpha-olefin polymers have a compatibility with processing oils that is not expected in the  
25 prior art because other olefin polymers do not exhibit such affinity. Specifically, polyethylene/ethylene methyl acetate copolymers, polyethylene/ethylene vinyl acetate copolymers and others are not even capable of being admixed with oil in large quantities. The failure

of other ethylene polymers would lead to the expectation that ethylene alpha-olefin polymers would not seem to be a source of improvement for current formulations of block copolymers with olefinic polymers where processing oil is needed to promote proper  
5 elastomerization of the block copolymers.

Nevertheless, it would be a great advance in the art if some way were to be found to strengthen block copolymers, particularly as to mechanical integrity, while not adversely affecting the softness of the elastomer.

10 Accordingly, it is an object of the present invention to provide a new composition having softness similar to that produced by block copolymer compositions with processing oil with out the attendant destruction of mechanical integrity.

Other objects will appear hereinafter.

### **DISCLOSURE OF THE INVENTION**

It has now been discovered that the above and other objects of the present invention may be accomplished in the following manner. Specifically, the present invention provides an elastomeric composition having a desired predetermined hardness.

The composition of this invention comprises a blend of a block copolymer having terminal polystyrene units and olefin elastomeric midblock units with an ethylene alpha-olefin polymer. The composition has a predetermined hardness that is at least 10 Shore A hardness units less than the Shore A hardness of the ethylene alpha-olefin polymers. Preferred ethylene alpha-olefin polymers have a hardness of from about 65 to about 85 Shore A, and yet the resulting composition surprisingly has a final hardness that is at least 10 Shore A units lower, and preferably is less than 50 Shore A.

The amount of ethylene alpha-olefin polymer in the composition can be any amount that provides mechanical integrity without increasing the hardness of the composition without it by any appreciable amount, say 5% to 10%. Preferred ratios of block copolymer to ethylene alpha-olefin polymer range from 1:10 to 10:1, with a ratio of 1:4 to 4:1 being most preferred.

The preferred ethylene alpha-olefin polymer is a substantially linear olefin polymer characterized as having

- a) a melt flow ratio,  $I_{10} / I_2 \geq 5.63$ ;
- b) a molecular weight distribution,  $M_w / M_n$ , defined by the equation  $M_w / M_n \geq (I_{10} / I_2) - 4.63$ ; and
- c) a critical shear stress at onset of gross melt fracture of greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>.



The substantially linear olefin polymer may be further characterized as a copolymer of ethylene with a C<sub>3</sub>-C<sub>20</sub> alpha-olefin. These ethylene alpha-olefin polymers are also known as metallocenes. The composition of this invention is useful with any of the block copolymer generally known, such as those having terminal polystyrene units and an olefin elastomeric midblock. Among these are those block copolymers selected from SEBS, SBS, SEPS and SIS.

A preferred composition also includes a quantity of processing oil, ranging from 0 to 1000 parts of oil per 100 parts of elastomer (phr) and preferably from about 20 to about 200 phr. The processing oils useful in the present invention may be any of the many processing oils that are used in combination with block copolymers of the type described above. Preferred due as much to availability and known results are oils selected from mineral oil, paraffinic oil and naphthenic oil and liquid polybutene oil, commonly known as Indopol® Oil, available from Amoco Chemical Company. All that is required of this component is that it be compatible with the block copolymer and function as expected as a plasticizing agent with that block copolymer.



### **BEST MODE FOR CARRYING OUT THE INVENTION**

As set forth above the present invention provides for surprising and unexpected improvement in block copolymer technology, in that it is now possible to have all of the desirable soft, elastomeric properties of block copolymers and also have mechanical integrity without compromise of these properties.

Specifically it is possible to have improved mechanical integrity without loss of softness, such that ethylene alpha-olefin polymers with hardness of 75 Shore A, for example, can be combined into elastomers having a desired hardness of 40 or 45 Shore A, with the resulting composition having improved mechanical integrity and a hardness virtually unchanged by the addition of the ethylene alpha-olefin polymer. It has been discovered that large quantities of ethylene alpha-olefin polymers can be formulated with block copolymers without materially changing the hardness of the block copolymer formulation. The resulting elastomeric composition has a predetermined hardness, depending on the needs of the end user. The addition of the ethylene alpha-olefin polymer does improve mechanical integrity keeps the hardness of the composition at least 10 Shore A units less than the hardness of the ethylene alpha-olefin polymer.

Block copolymers are, for the purpose of this invention, defined as block copolymers having terminal polystyrene units and olefin elastomeric midblock units. Among these are the block copolymers formed from ethylene, butylene block copolymers having terminal polystyrene units, known generally as SEBS copolymers. SEBS polymers are commercially available from Shell Chemical

Company under the trademark KRATON®. Block copolymers are described in U.S. Patent No. 3,686,364 and U.S. Patent No. 3,865,776, among others, are typical examples of the block copolymers contemplated by the present invention. The disclosure of  
5 both of these patents is incorporated herein by reference.

In the latter patent, assigned to Shell Oil Company, copolymers are described as having ethylene butylene central blocks of from 50% to 80% by weight of the copolymer molecule in approximately equal proportions of ethylene and butylene. The  
10 terminal blocks are substituted or unsubstituted polystyrene. Other thermoplastic elastomeric block copolymers with terminal polystyrene units (unsubstituted and substituted, such as polyalpha-methylstyrene and other mono-substituted polystyrenes) are also contemplated in the present invention, including butylene  
15 polymers (SBS), isobutylene polymers (SIS) and hydrogenated polyisoprene polymers (SEPS), all with terminal polystyrene end units.

The second component of the novel compositions of this invention are ethylene alpha-olefin polymers or metallocenes. These  
20 polymers are described in U.S. Patent No. 5,272,236 and U.S. Patent No. 5,278,272, both to Lai et al., both of which are incorporated herein by reference. It is intended that the general term ethylene alpha-olefin polymer be defined by the class of polymers described and disclosed in these two patents to Lai et al., and that the method  
25 of making the same be included in this description of the polymers. Preferred ratios of block copolymer to ethylene alpha-olefin polymer range from 1:10 to 10:1, with a ratio of 1:4 to 4:1 being most preferred.

Ethylene alpha-olefin polymers of the type included in the present invention have the following properties:

- a) a melt flow ratio,  $I_{10} / I_2 \geq 5.63$ ;
- b) a molecular weight distribution,  $M_w / M_n$ , defined by  
5 the equation  $M_w / M_n \geq (I_{10} / I_2) - 4.63$ , and
- c) a critical shear stress at onset of gross melt fracture of greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>.

Other properties of the substantially linear polymers defined as ethylene alpha-olefin polymers herein include:

- 10 a) a density of about 0.85 grams/cubic centimeter to about 0.97, and
- b) a melt index  $I_2$  from about 0.01 grams/10 minutes to about 1000 grams/10 minutes.

Preferably the melt flow ratio,  $I_{10} / I_2$ , is from about 7 to  
15 about 20. The molecular weight distribution ( $M_w / M_n$ ) is preferable less than about 5 especially from about 1.5 to about 2.5 and most preferably from about 1.7 to about 2.3.

The substantially linear polymers of the present invention can be homopolymers of C<sub>3</sub>-C<sub>20</sub> alpha-olefins, such as ethylene,  
20 propylene, 4-methyl-1-pentene, etc., or they can be interpolymers of ethylene with at least one C<sub>3</sub>-C<sub>20</sub> alpha-olefin and /or C<sub>3</sub>-C<sub>20</sub> acetylenically unsaturated monomer and/or C<sub>4</sub>-C<sub>18</sub> diolefins. The substantial linear polymers of the present invention can also be  
25 interpolymers of ethylene with at least one of the above C<sub>3</sub>-C<sub>20</sub> alpha-olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers. Methods for making the ethylene alpha-olefin polymers described here are set forth in detail in the aforementioned Lai et. al. patents.

Commercial quantities of the ethylene alpha-olefin polymers of the present invention are available from Dow Chemical Company of Midland, Michigan, under the trade name ENGAGE® polyolefin elastomers. In experiments described below, ENGAGE®  
5 polyolefin elastomers were employed. EG 8100 was used, having a hardness of 75 Shore A, while EG 8150, EG 8200, EP 8500 and others by Dow have also been found to be applicable to the present invention.

Another source of the ethylene alpha-olefin polymers or  
10 metallocenes of the present invention are available from Exxon Chemical Co. of Houston, Texas, under the trade name EXACT®. Exxon markets a series of these ethylene alpha-olefin polymers under the EXACT® trademark, using specific product designations such as 4023, 4024, 4033, 4031, 4042 and 5008.

15 The compositions of this invention may comprise merely the block copolymer described above and the second polymer described as an ethylene alpha-olefin polymer. It is also contemplated that a quantity of processing oil be added such that a preferred composition includes a plasticizing quantity of processing oil, ranging  
20 from 0 to 1000 parts of oil per 100 parts of elastomer (phr) and preferably from about 20 to about 200 phr. The processing oils useful in the present invention may be any of the many processing oils that are used in combination with block copolymers of the type described above. Preferred due as much to availability and known results are oils  
25 selected from mineral oil, paraffinic oil and naphthinic oil and liquid polybutene oil. All that is required of this component is that it be compatible with the block copolymer and function as expected as a plasticizing agent with that block copolymer.

The novel compositions of the present invention have a predetermined softness that is determined by the block copolymer and oil used in the composition. Amazingly the ethylene alpha-olefin polymers that form the remaining part of the invention compositions has virtually no affect on the hardness of the composition. Thus, for the first time it is possible to add a material that improves the mechanical integrity of a block copolymer elastomeric composition without adversely increasing the hardness of the elastomer. Typically the block copolymer will have a hardness of less than 50 Shore A, and even as low as 5 or 10 Shore A. The ethylene alpha-olefin polymers have a hardness ranging from about 65 to about 85 Shore A. The amount of ethylene alpha-olefin polymer in the composition can be any amount that provides mechanical integrity without increasing the hardness of the composition without it by any appreciable amount, say 5% to 10%.

When other olefinic polymers are added to block copolymers, such as, for example, polypropylene, the hardness increases generally with the increase in composition, as expected. Compositions with polypropylene and block copolymers such as SEBS tend to be balanced, trading softness for processability or mechanical integrity. As with any compromise, there are goals which are not achieved.

In order to demonstrate the efficacy of the present invention, a series of experiments were performed.

#### EXPERIMENT ONE

In order to demonstrate that the composition of the present invention has superior softness while also having good

mechanical integrity, a formulation according to the present invention was compared with a similar formulation using prior art polypropylene in place of the ethylene alpha-olefin polymer of the present invention. Formula A, below in Table I, represents the composition of the present invention. Formula B, also below in Table I, represents a prior art formulation using polypropylene. Formula C, also below in Table I, is a control having no additional polymer and being generally unsatisfactory as far as mechanical integrity. As can readily be seen, Formula A has both good processability and desired softness. Neither of the other products are satisfactory.

TABLE I

<u>COMPONENT</u>	<u>FORMULA A</u>	<u>FORMULA B</u>	<u>FORMULA C</u>
SEBS	100 parts	100 parts	100 parts
OIL	100 parts	100 parts	100 parts
PPE	NONE	50 parts	NONE
E A-E	50 parts	NONE	NONE
SHORE A	35	67	N/A
INTEGRITY	good	good	N/A

PPE represents polypropylene; E A-E represents ethylene alpha-olefin polymer, and N/A represents "not available" due to the product being inadequately formed using the same mixing techniques as the first two products.

EXPERIMENT TWO

In order to evaluate the present invention over a range of compositions falling within the scope of the invention, a number of



other formulations were prepared in which the amount of ethylene alpha-olefin polymer was varied with respect to the block copolymer, SEBS, to demonstrate the wide range of stability of the hardness of the compositions. Polypropylene (PPE) was included for ease of mixing and to permit a direct comparison across the entire range of variations. These results are presented below in Table II.

TABLE II

	<u>RUN NO.</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
10	OIL	100	100	100	100	100	100	100	100	100
	SEBS	100	75	50	25	0	100	100	100	100
	PPW	20	20	20	20	20	20	20	20	20
	EG 8100	100	100	100	100	100	75	50	25	0
	SHORE A	47	46	46	43	N/A	47	45	43	43
15	INTEGRITY	G	G	G	G	N/A	G	G	G	POOR

As can be seen, the present invention functions over a wide range of ratios between the block copolymer and the ethylene alpha-olefin. In Table II above, the ratio of the two ranges from 4:1 to 1:4 with no significant change in hardness or mechanical integrity. Note that run E was unable to formulate because the EG 8100 was unable to absorb oil and mix appropriately.

### EXPERIMENT THREE

Additional experiments were performed without any polypropylene present, to determine the direct effect of an ethylene alpha-olefin polymer having a Shore A hardness of 75 on a block copolymer. These results are presented below in Table III.



TABLE III

RUN NO.	J	K	L	M	N
OIL	100	100	100	100	--
5 SEBS	100	25	100	100	100
ENGAGE <sup>1</sup>	100	100	75	25	--
EXACT <sup>2</sup>	--	--	--	--	100
SHORE A	44	37	40	34	60
10 INTEGRITY	Good	Good	Good	Good	Good

1 = ENGAGE 8100 by Dow

2 = EXACT 5808 by Exxon

All of the above experimental runs shown in Table III are  
 15 illustrative of the surprising effectiveness of the present invention  
 functions over a range of ratios between the block copolymer and the  
 ethylene alpha-olefin polymer to produce soft elastomeric  
 compositions with good mechanical integrity even though the  
 ethylene alpha-olefin polymer has a much higher (and in many cases  
 20 unacceptable) hardness of 75 Shore A.

#### EXPERIMENT FOUR

The compositions of this invention were compared with  
 compositions made from other olefin polymers to demonstrate the  
 25 unexpected and superior properties of the present invention.  
 Specifically, compositions were mixed and formed into injection  
 molded samples for testing. Each composition was prepared in the  
 same manner and was tested using the same tests. The only variables

were the different olefin polymers and the ratios of block copolymer to olefin polymer as noted in the data presented below.

Table IV identifies the various compositions that were prepared for evaluation and Table V illustrates the results achieved in testing hardness, tensile strength and elongation.

TABLE IV

	<u>NO.</u>	<u>SEBS</u> parts	<u>OIL</u> parts	<u>2ND POLYMER</u> parts/name
10	a	100	100	25/ENGAGE <sup>a</sup>
	b	100	100	25/OPTEMA <sup>b</sup>
	c	100	100	25/ELVAX <sup>c</sup>
	d	100	100	25/ESCOR <sup>d</sup>
	e	100	100	100/ENGAGE <sup>a</sup>
15	f	100	100	100/OPTEMA <sup>b</sup>
	g	100	100	100/ELVAX <sup>c</sup>
	h	100	100	100/ESCOR <sup>d</sup>
	i	25	100	100/ENGAGE <sup>a</sup>
	j	25	100	100/OPTEMA <sup>b</sup>
20	k	25	100	100/ELVAX <sup>c</sup>
	l	25	100	100/ESCOR <sup>d</sup>

<sup>a</sup>ENGAGE<sup>®</sup> EG 8100 is an ethylene alpha-olefin polymer of this invention

25 <sup>b</sup>OPTEMA<sup>®</sup> TC 115 from Exxon is a PE/EMA copolymer

<sup>c</sup>ELVAX<sup>®</sup> 550 from DuPont is an PE/EVA copolymer

<sup>d</sup>ESCOR<sup>®</sup> ATX 320 from Exxon is a PE/EMA/EAA terpolymer

TABLE V

<u>NO.</u>	<u>DURO</u> shore A	<u>TENSILE</u> psi	<u>% decrease</u>	<u>ELONGATION</u> % to break	<u>% decrease</u>
1	31	434	control	552	control
5 2	41	285	-34%	238	-57%
3	39	294	-32%	243	-56%
4	32	198	-54%	349	-37%
5	46	815	control	759	control
6	61	592	-27%	337	-56%
10 7	59	558	-32%	503	-34%
8	52	474	-42%	390	-49%
9	39	good integrity			
10	60	n/a - excessive oil bleeding			
11	58	n/a - excessive oil bleeding			
15 12	48	n/a - excessive oil bleeding			

As can readily be seen from the data presented in Table V, the compositions of this invention as identified by numbers 1, 5 and 9 produced surprising and superior results. Specifically, the hardness, tensile strength and elongation are all unexpectedly superior to the same values for those compositions using other olefin polymers. In fact, only the present invention was even capable of forming an elastomer composition when higher levels of oil were used, such as in numbers 9 through 12.

25

EXPERIMENT FIVE

Because composition 9 of Experiment Four possessed excellent integrity as an elastomer, whereas the prior art materials were unable to form due to excessive and undesirable oil bleeding, other experiments were performed to demonstrate another

surprising and unexpected advantage of the present invention. Increased amounts of oil have been added up to 1000 phr in various formulations.

Presented below in Table VI are test results of various formulations in which the amount of oil is increased substantially and two different ethylene alpha-olefin polymers are used in varying proportions. The increased oil produced very soft materials that may be formulated into a variety of products where soft, almost gel like materials are needed. Strength is measured in 300% modulus, which is the strain in psi at 300% elongation.

TABLE VI

RUN NO.	AA	BB	CC	DD	EE
OIL	330	330	330	330	200
SEBS	100	25	100	25	25
ENGAGE <sup>1</sup>	10	--	25	--	100
EXACT <sup>2</sup>	-	10	--	25	--
SHORE A	4	3	7	3	10
Modulus <sup>3</sup>	41	20	41	33	42

1 = ENGAGE 8100 by Dow

2 = EXACT 5808 by Exxon

3 = 300% Modulus, psi

N/A = not available due to excessive elongation

The composition of this invention can be processed into a wide variety of products in many industries, where soft and strong elastomeric materials are needed. As is normally the case, fillers, anti-oxidants, dyes, processing aids, and other ingredients may be

added as in conventional designs without adversely affecting the surprising and unexpected results of the present invention.

While particular embodiments of the present invention have been illustrated and described, it is not intended to limit the  
5 invention, except as defined by the following claims.

**CLAIMS**

1. An elastomeric composition having a desired predetermined hardness, comprising a blend of:
  - a block copolymer having terminal polystyrene units and olefin elastomeric midblock units; and
  - 5 an ethylene alpha-olefin polymer, said polymer being a substantially linear olefin polymer characterized as having
    - a) a melt flow ratio,  $I_{10}/I_2 \geq 5.63$ ;
    - b) a molecular weight distribution,  $M_w/M_n$ , defined by the equation  $M_w/M_n \geq (I_{10}/I_2) - 4.63$ , and
    - 10 c) a critical shear stress at onset of gross melt fracture of greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>.
2. The composition of claim 1 wherein said block copolymer  
15 is selected from SEBS, SBS, SEPS and SIS.
3. The composition of claim 1 wherein the substantially linear olefin polymer is further characterized as a copolymer of  
20 ethylene with a C<sub>3</sub>-C<sub>20</sub> alpha-olefin.
4. The composition of claim 1 which further includes a plasticizing amount of processing oil in an amount ranging from 0 to  
25 1000 parts of oil per 100 parts of elastomer.

5. The composition of claim 4 wherein said processing oil is selected from mineral oil, paraffinic oil and naphthenic oil and liquid polybutene oil and the amount ranges from 20 to 200 parts of oil per  
5 100 parts of elastomer.

6. The composition of claim 1, wherein the ratios of block copolymer to ethylene alpha-olefin polymer range from 1:10 to 10:1.  
10

7. A method of forming an elastomeric composition having a desired predetermined hardness, comprising the steps of:  
admixing a block copolymer having terminal polystyrene  
15 units and olefin elastomeric midblock units with an ethylene alpha-olefin polymer, said polymer being a substantially linear olefin polymer characterized as having  
a) a melt flow ratio,  $I_{10} / I_2 \geq 5.63$ ;  
b) a molecular weight distribution,  $M_w / M_n$ , defined by  
20 the equation  $M_w / M_n \geq (I_{10} / I_2) - 4.63$ , and  
c) a critical shear stress at onset of gross melt fracture of greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>; and  
forming said admixture into said elastomeric composition.

25

8. The method of claim 7 wherein said block copolymer is selected from SEBS, SBS, SEPS and SIS.



9. The method of claim 7 wherein the substantially linear olefin polymer is further characterized as a copolymer of ethylene with a C<sub>3</sub>-C<sub>20</sub> alpha-olefin.

5

10. The method of claim 7 which further includes adding a plasticizing amount of a processing oil in an amount ranging from 0 to 1000 parts of oil per 100 parts of elastomer.

10

11. The method of claim 10, wherein said processing oil is selected from mineral oil, paraffinic oil and naphthinic oil and liquid polybutene oil and the amount ranges from 20 to 200 parts of oil per 100 parts of elastomer.

15

12. The method of claim 7, wherein the ratios of block copolymer to ethylene alpha-olefin polymer range from 1:10 to 10:1.

20

## AMENDED CLAIMS

[received by the International Bureau on 15 August 1995 (15.08.95);  
original claims 1, 2, 7 and 8 amended; remaining claims unchanged (2 pages)]

1. An elastomeric composition having a desired predetermined hardness, comprising a blend of:
  - a block copolymer having terminal polystyrene units and hydrogenated ethylene-olefin elastomeric midblock units;
  - 5 an ethylene alpha-olefin polymer, said polymer being a substantially linear olefin polymer characterized as having
    - a) a melt flow ratio,  $I_{10}/I_2 \geq 5.63$ ;
    - b) a molecular weight distribution,  $M_w/M_n$ , defined by the equation  $M_w/M_n \geq (I_{10}/I_2) - 4.63$ , and
    - 10 c) a critical shear stress at onset of gross melt fracture of greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>.
2. The composition of claim 1 wherein said block copolymer  
15 is selected from SEBS and SEPS.
3. The composition of claim 1 wherein the substantially linear olefin polymer is further characterized as a copolymer of  
20 ethylene with a C<sub>3</sub>-C<sub>20</sub> alpha-olefin.
4. The composition of claim 1 which further includes a plasticizing amount of processing oil in an amount ranging from 0 to  
25 1000 parts of oil per 100 parts of elastomer.

5. The composition of claim 4 wherein said processing oil is selected from mineral oil, paraffinic oil and naphthinic oil and liquid polybutene oil and the amount ranges from 20 to 200 parts of oil per  
5 100 parts of elastomer.

6. The composition of claim 1, wherein the ratios of block copolymer to ethylene alpha-olefin polymer range from 1:10 to 10:1.  
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7. A method of forming an elastomeric composition having a desired predetermined hardness, comprising the steps of:  
admixing a block copolymer having terminal polystyrene  
15 units and hydrogenated ethylene-olefin elastomeric midblock units with an ethylene alpha-olefin polymer, said polymer being a substantially linear olefin polymer characterized as having  
a) a melt flow ratio,  $I_{10}/I_2 \geq 5.63$ ;  
b) a molecular weight distribution,  $M_w/M_n$ , defined by  
20 the equation  $M_w/M_n \geq (I_{10}/I_2) - 4.63$ , and  
c) a critical shear stress at onset of gross melt fracture of greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>; and  
forming said admixture into said elastomeric composition.

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8. The method of claim 7 wherein said block copolymer is selected from SEBS and SEPS.

## STATEMENT UNDER ARTICLE 19

Replacement claims 1, 2, 7 and 8 conform to like claims pending in the corresponding United States application in which the block copolymer has been limited to SEBS type materials and do not cover SBS types.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/04280

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :CO8L 53/00, 53/02

US CL :524/505, 534

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/505, 534

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	WO, A, WO 94/18263 (EXXON CHEMICAL PATENTS INC.) 18 August 1994, page 11, lines 5-10 and page 11 line 23.	1-12
X	US, A, 5,272,236 (LAI ET AL) 21 December 1993, col. 14, line 35, and claim 1.	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

17 MAY 1995

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